(12) UK Patent Application (19) GB (11) 2 264 558 (13) A

(43) Date of A publication 01.09.1993

(21) Application No 9303163.1

(22) Date of filing 17.02.1993

(30) Priority data
(31) 9204064 (32) 26.02.1992 (33) GB

(71) Applicant
The British Petroleum Company p.l.c.

(Incorporated in the United Kingdom)

Britannic House, 1 Finsbury Circus, London, EC2M 7BA, United Kingdom

(72) Inventor
Evangelos Theocharous

(74) Agent and/or Address for Service
Edward Terrence Ryan
BP International Limited,
Patents and Licensing Division, Chertsey Road,
Sunbury-on-Thames, Middlesex, TW16 7LN,
United Kingdom

(51) INT CL[5]
G01N 21/64, B07C 5/342

(52) UK CL (Edition L)
G1A AA4 AA6 AD4 AMK AP16 AP17 AP6 AP9 AR6 AR7 AS13 AS4 AT14 AT23 AT3
U1S S1253 S1442 S1529 S1878

(56) Documents cited
GB 2234347 A EP 0476416 A EP 0466474 A
US 4127773 A US 3912928 A

(58) Field of search
UK CL (Edition L) G1A ACJ AMH AMK
INT CL[5] B07C 5/342, G01N 21/64
Online database: WPI

(54) Method of identifying polymer materials

(57) At least one material capable of fluorescing in the far red or near infrared region is added to a polymer. A polymer sample 2 may be subsequently identified by illumination from a laser source 1 at wavelengths in the far red or near infrared suitable for exciting the fluorescent material, and determining the presence of the material by spectroscopic means 6 to identify the polymer. The polymer may be labelled with at least two fluorescent materials, the materials being present in a predetermined weight ratio whereby the ratio of the fluorescence intensities observed for each material is proportional to the predetermined weight ratio.

The fluorescent materials may be dyes or rare earth compounds added to the polymer in solution or as sub-micron particles in a concentration from 0.001 to 1 ppm.

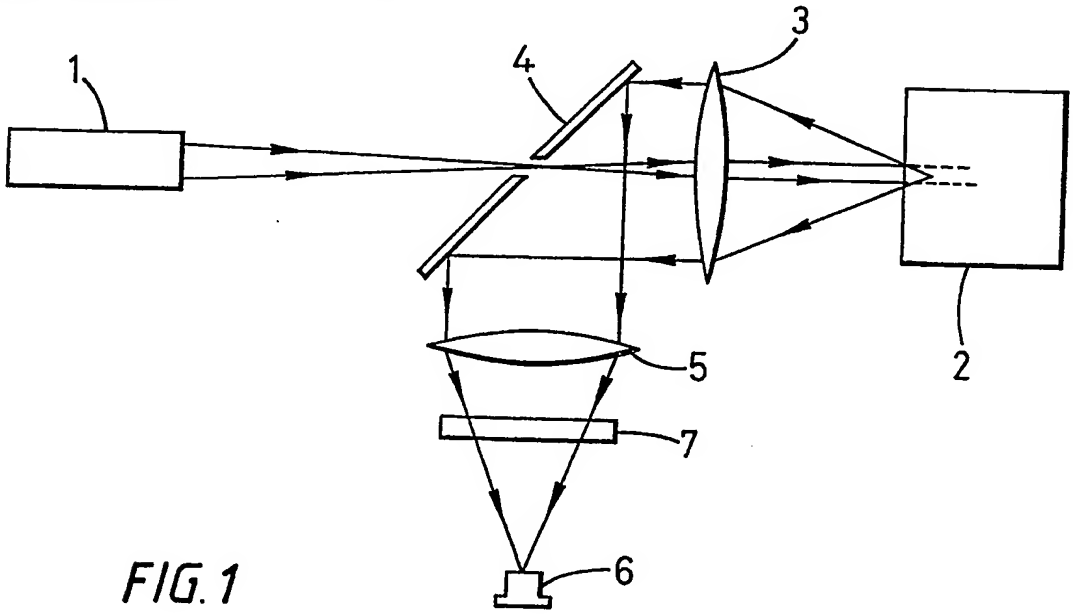

FIG. 1

GB 2 264 558 A

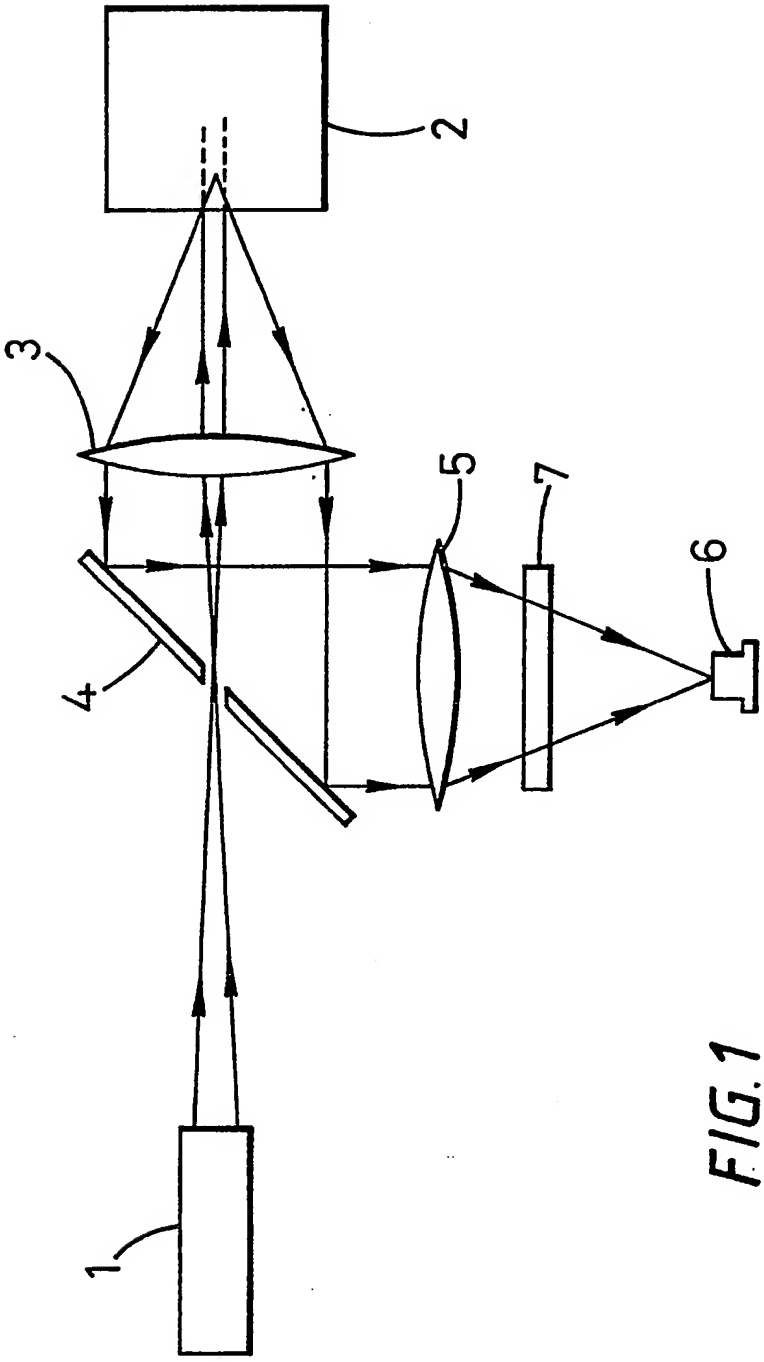

FIG.1

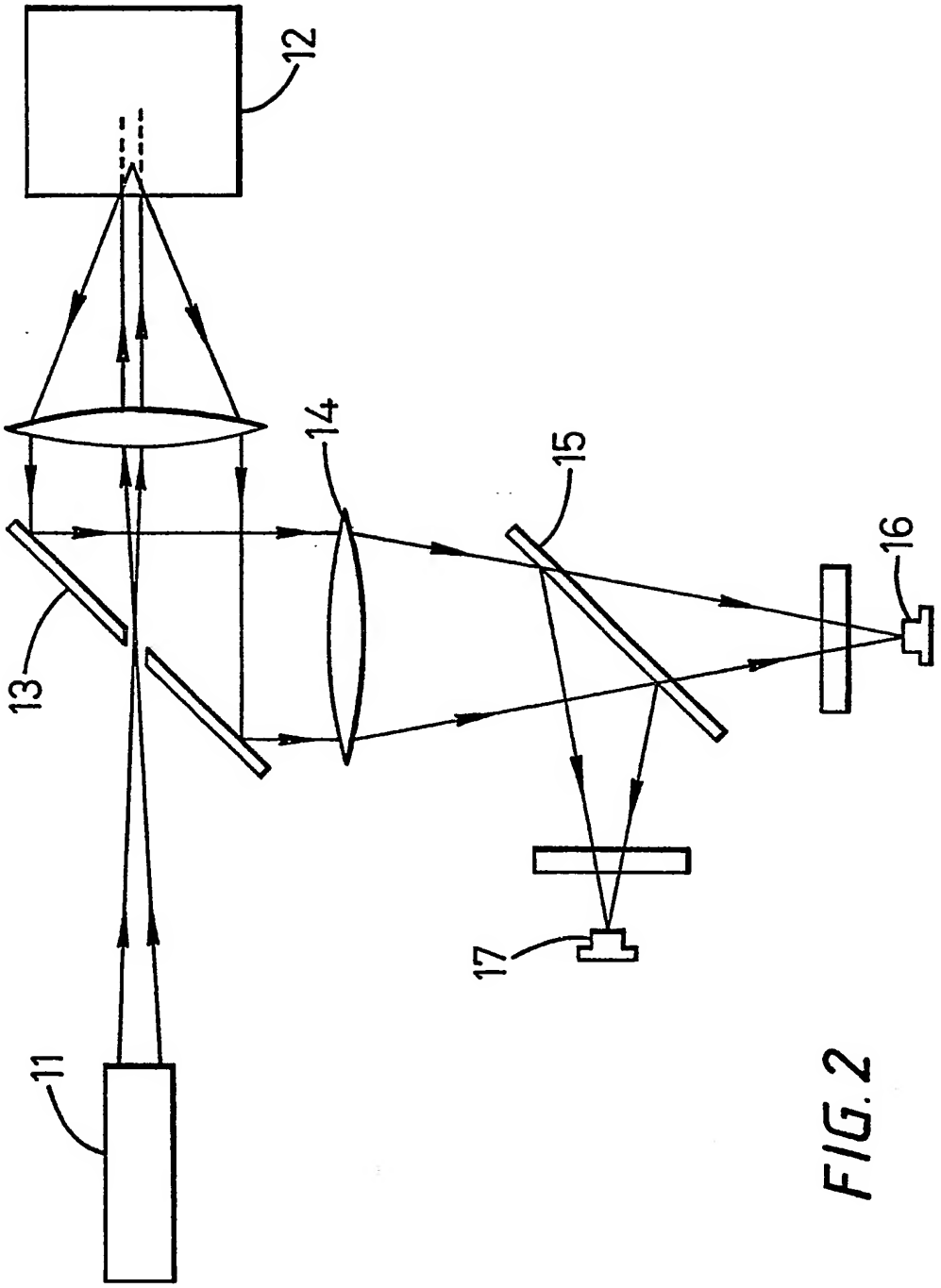

FIG. 2

METHOD OF IDENTIFYING POLYMER MATERIALS

The present invention relates to a method of identifying polymer materials in particular to a method of identifying polymers by use of near infrared (NIR) fluorescence spectroscopy.

Polymer waste particularly plastic waste forms approximately 7% of domestic waste and can be higher in some industrial areas. A major problem with the recycling of plastic waste is the absence of precise and efficient systems to separate out individual plastic materials from a mixed waste stream.

Plastic waste is diverse and may include coloured or opaque high density polyethylene bottles or containers, clear or tinted polyethylene terephthalate cups as well as a diversity of polyvinyl chloride bottles.

At present various methods for identifying and sorting plastic waste have been used. Procedures which rely on manual sorting tend to be unreliable due to eyesight, poor attention span and slowness. More recently techniques involving electromagnetic spectroscopy have been developed but these tend to be complex and costly and impractical for commercial use.

To enable efficient recycling there is a need to identify a low cost, fast and reliable method of identifying plastics which can be used to separate various families of plastics from mixed waste.

Fluorescence spectroscopy is a well established analytical technique capable of providing high sensitivity combined with good selectivity. Fluorescent light has a different wavelength compared to the excitation light. The fluorescent light can therefore be

spectrally filtered and monitored above a zero background level. This allows fluorescence spectroscopy to be used to detect very low concentrations.

Unfortunately in some circumstances many species fluorscence when excited by light of high photon energy, for example UV light, and this can be a serious drawback in signal detection because the detection of a fluorescence signal cannot be unambiguously assigned to the species being detected.

Polymers such as polyethylene do not fluoresce when excited with far red or near infrared (NIR) light.

We have now found that by using materials which fluoresce in the far red or near infrared region of the spectrum polymers may be labelled to enable their identification. In this way the recycling of polymer waste may be facilitated by using very low concentrations of such fluorescent materials.

Thus according to the present invention there is provided a method for identifying a polymer, said method comprising the steps of:

(a) adding at least one material capable of fluorescing in the far red or near infrared region to the polymer,

(b) exposing the polymer to a laser source at wavelengths in the far red of near infrared suitable for exciting said material, and

(c) determining the presence of said material by spectroscopic means to identify said polymer.

Suitable materials include dyes which fluoresce at wavelengths in the range 600 to 1000 nm, in particular in the range 700-900 nm.

Other suitable materials include rare earth compounds.

Diode lasers are particularly suitable for use in the method of the present invention having the advantages of low cost, small size and high reliability.

The presence of fluorescing materials in a polymer may suitably be detected by means of a silicon photodetector.

The fluorescence detected from the polymer may suitably be displayed as a spectrum of fluorescence signal against wavelength.

The method of the present invention is particularly suitable

for use in the labelling of plastic materials for example in the recycling of plastics.

Since plastic materials do not fluoresce significantly when illuminated with near infrared radiation the method of the present invention has the advantage of requiring very low concentrations of dyes for labelling applications.

Typical concentrations are those in the range 0.001 to 1 ppm.

For recycling applications where it is necessary to be able to identify a number of polymers from a group of polymers the preferred number of fluorescent materials present in each polymer is two.

For this application the fluorescent materials chosen are those in which their fluorescence spectra do not overlap. The resulting spectra may be separated by suitable optical filtering and the fluorescence strength of each material measured.

Each polymer may be labelled with the same fluorescent materials but at different relative concentrations. The ratio of the fluorescence intensities of the two materials may be correlated with the ratio of the weights of the materials present in the polymer and can be used to provide unambiguous labelling of a large number of polymers.

In this way different polymers, blends of polymers or polymer compositions may each be given a unique label based on the relative concentrations of the fluorescent materials present.

The presence of the labelled polymer or labelled composition may thereby be detected by the method of the present invention.

Thus according to another aspect of the present invention there is provided a method for identifying a polymer said method comprising the steps of

(a) labelling said polymer by adding at least two materials capable of fluorescing in the far red or near infrared region to the polymer, said materials being present in a predetermined weight ratio,

(b) exposing the polymer to a laser source at wavelengths in the far red or near infrared suitable for exciting said materials, and

(c) determining the presence of said labelled polymer by

spectroscopic means whereby the ratio of the fluorescence intensities observed for each material is proportional to said predetermined weight ratio.

If required three or more fluorescent materials may be incorporated in each polymer and identified in a similar way.

By using more than one fluorescent material, factors such as the obscuration of the polymer sample due to dirt or container scattering, fluctuations in the excitation source or changes in the position of the sample which may give rise to a reduction in the strength of the fluorescent signal, may be reduced.

Since the fluorescent materials employed have broad absorption bands the fluorescence of two materials can be excited by use of a single source emitting at a suitable wavelength.

The fluorescent materials may suitably be added to the polymer in solution before the polymer solidifies. Alternatively they may be first incorporated in solid particles of sub-micron diameter which are subsequently added to the polymer solution.

The present invention is further illustrated with reference to the accompanying Figures wherein:

Figure 1 represents an arrangement suitable for identifying a polymer, and

Figure 2 represents an arrangement whereby the presence of two fluorescent materials in a polymer may be identified.

In Figure 1 a diode laser (1) emitting at a wavelength of 670nm is used to illuminate a polymer sample (2) incorporating a suitable dye. The laser is recollimated by a glass lens (3) before entering the sample. Some of the fluorescence generated along with some of the reflected and scattered laswer light is recollimated by lens (3) reflected by an aluminium coated mirror (4) positioned at 45° to the laser output, and focused by means of lens (5) onto a silicon photodetector (6). A long pass filter (7) transmitting above 720nm is used to block the 670nm reflected and scattered light.

The photodetector output is amplified using a two-stage single chip amplifier.

In Figure 2 the fluorescence spectra from a sample

incorporating two dyes are recorded by using two detectors.

The output from the laser (11) after reflection by the sample (12) and mirror (13) is passed through lens (14) and split by the beamsplitter (15) before passing to the photodetectors (16) and (17).

Claims:

1. A method for identifying a polymer, said method comprising the steps of:

(a) adding at least one material capable of fluorescing in the far red or near infrared region to the polymer.

(b) exposing the polymer to a laser source at wavelengths in the far red of near infrared suitable for exciting said material, and

(c) determining the presence of said material by spectroscopic means to identify said polymer.

2. A method according to claim 1 in which the material capable of fluorescing in the far red or near infrared region to the polymer is a dye or a rare earth compound.

3. A method according to claim 2 in which the dye or rare earth compound is present in a concentration of from 0.001 to 1ppm.

4. A method according to any one of the preceding claims in which the laser source is a diode laser.

5. A method according to any one of the preceding claims in which the presence of said material is determined by means of a silicon photodetector.

6. A method for identifying a polymer, said method comprising the steps of

(a) labelling said polymer by adding at least two materials capable of fluorescing in the far red or near infrared region to the polymer, said materials being present in a predetermined weight ratio.

(b) exposing the polymer to a laser source at wavelengths in the far red or near infrared suitable for exciting said materials, and

(c) determining the presence of said labelled polymer by spectroscopic means whereby the ratio of the fluorescence intensities observed for each material is proportional to said predetermined weight ratio.

7. A method according to claim 6 in which the materials capable of fluorescing are added to the polymer in solution.

8. A method according to claim 6 in which the materials capable of fluorescing are added to the polymer as solid particles of sub-micron diameter

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number
GB 9303163.1

Relevant Technical fields

(i) UK Cl (Edition L) G1A (ACJ AMH AMK)

(ii) Int Cl (Edition 5) B07C 5/342
G01N 21/64

Search Examiner
JOHN CAGE

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search
25 MARCH 1993

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	GB 2234347 A	(BXL PLASTICS) whole document	1
A P	EP 0476416 A2	(BAYER AG)	
X	EP 0466474 A1	(DOWTY SEALS) whole document	1
X	US 4127773	(WEST) see column 3 lines 7-48	1, 6
X	US 3912928	(RUSH) see column 4 lines 14-34	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

Published 1993 at The Patent Office, Concept House, Cardiff Road, Newport, Gwent NP9 1RH. Further copies may be obtained from Sales Branch, Unit 6, Nine Mile Point, Cwmfelinfach, Cross Keys, Newport, NP1 7HZ. Printed by Multiplex techniques ltd, St Mary Cray, Kent.